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## DETERMINATION OF MASS TRANSFER RATES IN WETTED AND NON-WETTED MICROPOROUS MEMBRANES

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**Abstract**—The mass transfer resistance of microporous membranes placed between a gas and a liquid phase was studied for both wetted and non-wetted membranes. It was found that the mass transfer coefficient can be described according to the film model in which the porosity of the membrane and the tortuosity of the pores is incorporated. For the non-wetted membranes (mean pore diameter of 0.1  $\mu\text{m}$ ), the Knudsen and continuum diffusion must be taken into account. No difference was observed in the values of the liquid-phase mass transfer coefficients between systems with and without a membrane at the gas–liquid interface, despite the different hydrodynamic situation at the interface. The influence of a chemical equilibrium reaction on the mass transfer through a wetted membrane was analysed mathematically (two-film concept). With this model the tortuosity factor of the membrane was calculated from experimentally determined fluxes.

### 1. INTRODUCTION

Until a few years ago, microporous hollow-fibre membrane modules were only used for filtration purposes. However, Qi and Cussler (1985b, c) and Cooney and Jackson (1989) have shown that the use as gas–liquid contactors in gas absorption processes is also feasible. The membrane acts as a fixed interface and keeps the gas and liquid phase separated while the transport of reactants/products can take place through the membrane. Depending upon the membrane material, the liquid and the pressure of both phases, the pores of the membrane are filled with either liquid or gas. These two types of membranes are often referred to as wetted and non-wetted, respectively.

Hollow-fibre membrane modules offer some significant advantages compared to conventional absorbers like bubble columns, tray columns or packed beds. In a hollow-fibre membrane module the interfacial area between the gas and liquid phase is formed by the membranes, while in the conventional absorbers it is mainly determined by the direct interaction between gas and liquid flow. The amount of interfacial area that can be realised in hollow-fibre membrane modules is much larger than the values encountered in the conventional contactors [maximum of 1000  $\text{m}^2/\text{m}^3$ , Laurent and Charpentier, (1974) and van Landeghem (1980)]. For the hollow-fibre modules, numbers of 10,000  $\text{m}^2/\text{m}^3$  are reported by Matson *et al.* (1983).

Another advantage of the hollow-fibre membrane module (HFMM) is its larger operation flexibility because the gas and liquid flow are separated by the membrane and, therefore, no mutual influence is pos-

sible. In conventional absorbers, however, operation flexibility is severely limited by phenomena like flooding, loading, weeping, entrainment, etc.

The mass transfer rates in the module, however, are limited by the mass transfer resistances in the gas and liquid phase and the additional resistance introduced by the membrane wall. In the conventional contactors the gas and liquid flow are often turbulent, while, in modules with small fibres and small channels between the fibres, the gas and liquid flow is usually laminar. Mass transfer resistances are generally lower in turbulent than in laminar flow and, therefore, it is expected that the mass transfer rate in the gas and liquid on both sides of the membranes in the module will be lower. Also the additional mass transfer resistance of the membrane (which can be regarded as a stagnant layer) reduces the mass transfer rate.

In the present study the additional mass transfer resistance of the membrane will be studied for both wetted and non-wetted membranes. The experiments are carried out in a model reactor consisting of two well-stirred compartments separated by a flat membrane. The results are compared with the mass transfer coefficients for systems without a membrane at the gas–liquid interface.

### 2. THEORY

Mass transfer in the membrane system of the present study can be described with a resistances in series model. This means that the overall mass transfer coefficient can be related to the sum of the partial resistances in the gas, the membrane and the liquid phase,  $k_G$ ,  $k_M$  and  $k_L$ , respectively. Equation (1a) is valid in a system with a non-wetted membrane:

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{1}{k_{M,nw}} + \frac{1}{mk_L} \quad (1a)$$

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For wetted membranes  $K_G$  is expressed in eq. (1b):

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{1}{mk_{M,w}} + \frac{1}{mk_L} \quad (1b)$$

Mass transfer is determined by diffusion and convection. Different models have been proposed to relate mass transfer with these two effects.

The boundary layer model (Leveque, 1928) describes a process where convection and diffusion are both present. In this model the existence of a layer is assumed between the bulk and the interface with a constant velocity gradient, while the velocity at the interface is zero. The mass transfer coefficient is proportional to  $D^{2/3}$ .

In the surface renewal models [e.g. Higbie (1935) and Danckwerts (1951)] it is proposed that finitely small fluid elements remain for a certain contact time at the interface and that the soluble components are transported by means of nonstationary diffusion. The mass transfer coefficient is proportional to the square root of the diffusion coefficient.

In the porous structure of a microporous membrane the convection can be neglected. The film model (Whitman, 1923) describes the molecular transport and the mass transfer coefficient can be calculated from eq. (2):

$$k_M = \frac{D_{i,e}}{d} = D_i \frac{\varepsilon}{d\tau} \quad (2)$$

Owing to the porosity of the membrane and the tortuosity of the pores, the diffusion coefficient,  $D_i$ , can be affected, resulting in an effective diffusion coefficient,  $D_{i,e}$ . When  $\varepsilon$ ,  $\tau$  and the thickness of the membrane are known, eq. (2) can also be used to calculate diffusion coefficients from mass transfer experiments in diaphragm cells [see e.g. Stokes (1950), Takeuchi *et al.* (1975) and Takahashi and Kobayashi (1982)].

In porous structures two types of diffusion can be distinguished: the continuum diffusion, which is determined by the interactions of the different molecules, and the Knudsen diffusion when the interactions of the molecules with the walls of the pores are dominating. Generally, the Knudsen diffusion is important only in small gas-filled pores ( $d_p < 0.1 \mu\text{m}$ ). In a liquid phase the number density of molecules is much higher; therefore, the interaction of liquid molecules with the walls of the porous structure usually can be neglected.

In the intermediate region, where both types of diffusion play a role, the diffusion coefficient can be related to the continuum and the Knudsen diffusion coefficient. In the case of a binary mixture,  $D_i$  is calculated from eq. (3):

$$\frac{1}{D_i} = \frac{1}{D_{i,j}} + \frac{1}{D_{K,i}} \quad (3)$$

The continuum diffusion coefficient in a gas phase can be calculated from the kinetic gas theory. The Knudsen diffusion coefficient is related to the inverse of the square root of the molecular weight:

$$D_{K,i} = \frac{4}{3} Q \sqrt{\frac{8RT}{\pi M}} \quad (4)$$

where  $Q$  is a constant, depending upon the geometry of the pores and the scattering laws, which describe the interaction between the molecules and the porous structure (Mason and Malinauskas, 1983).

In the literature a number of studies are published in which the mass transfer coefficient of flat membranes was measured. By choosing the proper experimental conditions, the mass transfer resistances in the phases outside the membrane can be made negligible. In a liquid-liquid extraction system Sirkar and co-workers investigated the mass transfer in wetted membranes (Kiani *et al.*, 1984; Prasad and Sirkar, 1988). The mass transfer parameters of non-wetted membranes were measured by Qi and Cussler (1985a). However, from the high mass transfer resistances they observed during their experiments it seems that their non-wetted membranes were wetted.

In HFMM it is less easy to reduce the resistances of the phases on both sides of the membrane. Therefore, the mass transfer in the membrane was only estimated from overall results (Qi and Cussler, 1985b, c; Cooney and Jackson, 1989).

In the present study the mass transfer coefficients of both wetted and non-wetted membranes are measured. Because diffusion takes place in gas- and liquid-filled pores, the diffusion coefficient was varied over a wide range.

### 3. EXPERIMENTAL

#### 3.1. Experimental set-up

The experiments with both wetted and non-wetted membranes were performed in a stirred cell with a flat horizontal membrane at the interface. The experimental set-up is shown in Fig. 1. In the reactor both phases could be stirred independently. The speed of the gas-phase stirrer (3 blades of 0.045 m diameter) could be varied from 5 to 35 rps. The liquid-phase stirrer consisted of two blades, also 0.045 m diameter and its speed could be varied from 0.5 to 7 rps. Both stirrers were magnetically driven to avoid leakage from the cell. The volumes of the gas and liquid compartment were equal,  $0.75 \times 10^{-3} \text{ m}^3$ . The membranes were glued between metal ring, resulting in an effective interfacial area of  $5 \times 10^{-4} \text{ m}^2$  which is identical to the cross-sectional area. No allowance has been made for the porosity of the membrane. The reactor was placed in an isothermal waterbath in order to maintain a constant temperature of 298 K.

The non-wetted membranes used were supplied by Enka (Accurel, polypropylene) with average pore diameter of 0.1 and 0.2  $\mu\text{m}$ , thickness 145 and 90  $\mu\text{m}$ , porosity 70–75%. Wetted membranes were purchased from Pall (nylon 66), with average pore diameter 0.1  $\mu\text{m}$ , thickness 100  $\mu\text{m}$ , porosity 70%.

#### 3.2. Experiments with non-wetted membranes

As mentioned before in determining the mass transfer resistance of the non-wetted membranes, the resist-

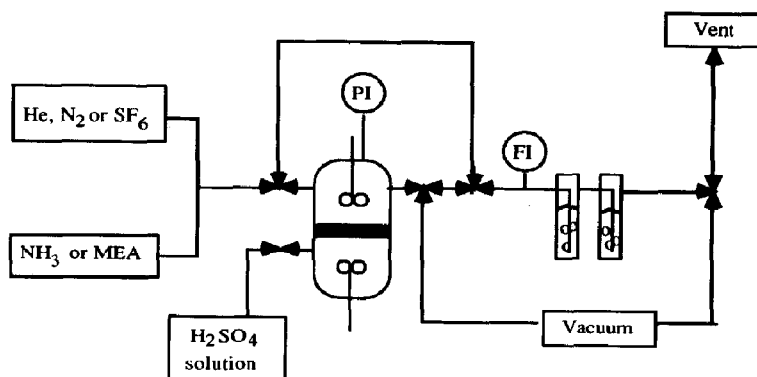


Fig. 1. Experimental set-up.

ances of the gas and liquid phase must be negligible compared to that of the membrane. The resistance of the liquid phase was reduced according to the methods proposed by Danckwerts (1970). The transferred component has a high solubility in the liquid (large  $m$ ), the stirrer speed is increased (larger  $k_L$ ) and in the liquid the solute reacts extremely fast and, therefore, the mass transfer rate is substantially enhanced [resulting in an effective larger  $k_L$ , eq. (1)]. The resistance in the gas phase was reduced by increasing the stirrer speed. The resistance of the membrane could be changed by the total number of membranes between the gas and the liquid.

Different gas mixtures were used in the absorption experiments in order to vary the diffusion coefficient at atmospheric pressure. Ammonia or mono-ethylamine (MEA) were absorbed from an inert gas phase, He, N<sub>2</sub> or SF<sub>6</sub>, into an aqueous solution of sulphuric acid, 2 M. A variation of the continuum gas-phase diffusion coefficient by a factor of 15 could be realised. The physico-chemical properties of the experimental systems were calculated according to the correlations in Reid *et al.* (1988). Owing to the difference in molar weight the ratio of the Knudsen diffusion coefficients of ammonia and MEA is 1.6.

Two different experimental techniques, batchwise and stationary absorption experiments, were used to measure mass transfer coefficients.

**3.2.1. Experiments with a batchwise-operated gas phase.** In these experiments, first, the liquid compartment was filled with the acidic solution. Next, the gas compartment was evacuated by a vacuum pump. During this evacuation, dissolved gases in the liquid were removed. The gas compartment was filled with nitrogen to about 100 kPa. Next, a small amount of ammonia (5–10 kPa) was added to the nitrogen. The absorption rate of ammonia into the liquid was measured by a pressure transducer connected to the gas compartment.

The mass balance for ammonia yields an expression for the overall mass transfer coefficient [eq. (5)], in which the concentration of the transferred component

in the bulk of the liquid is assumed to be equal to zero because of the irreversible neutralisation reaction:

$$\ln \left( \frac{P_{\text{NH}_3,0}}{P_{\text{NH}_3,t}} \right) = \frac{K_G A t}{V_G} \quad (5)$$

In these experiments the initial pressure of NH<sub>3</sub> turned out to be critical for a correct measurement of the mass transfer coefficient. If too much NH<sub>3</sub> was present, the absorption and reaction heat of NH<sub>3</sub> generated evaporation of water into the gas phase. The flow of water vapour into the gas phase disturbed the absorption rate of ammonia and the pressure decrease was no longer a direct measure of the NH<sub>3</sub> absorption. Next to this, the gas phase became supersaturated with water compared to the wall temperature and, therefore, condensation of water occurred which could be observed visually. In the next experiment ammonia also absorbed in this condensed liquid, which affected the absorption rate owing to the high solubility of NH<sub>3</sub> in water. In the experiments with an initial ammonia pressure less than 10 kPa, no condensation was observed visually. Therefore, it was assumed that the results of these experiments were not influenced by the heat effect of the absorption.

**3.2.2. Experiments with a continuous gas flow.** The cell was filled with liquid as mentioned in the previous section. For the gas phase the inert and the reactive gas were mixed to a desired composition with thermal mass flow controllers and the mixture was led through the reactor at  $10\text{--}15 \times 10^{-6} \text{ m}^3/\text{s}$ . Samples of inlet and outlet streams were led through several gas bubblers filled with an acidic solution to remove the remaining basic components in the gas mixture completely. By means of a titration, the concentrations of reactive component could be determined.

A mass balance over the gas phase of the stirred cell, which was considered as ideally mixed, yields the overall mass transfer coefficient:

$$K_G = \frac{1}{A} \left( \Phi_{G,\text{in}} \frac{C_{G,\text{in}}}{C_{G,\text{out}}} - \Phi_{G,\text{out}} \right) \quad (6)$$

### 3.3. Experiments with wetted membranes

In order to measure the mass transfer resistance of the wetted membrane, pure gases were used and, therefore, the gas-phase resistance can be neglected. The resistance in the liquid phase was reduced by increasing the liquid stirrer speed.

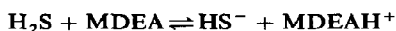
The absorption of CO<sub>2</sub> into water was studied. In this case the gas and liquid were operated batchwise and the pressure decrease was measured as a function of time. Owing to this operation, saturation was reached eventually.

For the absorption the mass balance for carbon yields

$$\ln \left( \frac{P_{\text{CO}_2} - P_{\text{CO}_2,\infty}}{P_{\text{CO}_2,0} - P_{\text{CO}_2,\infty}} \right) = - \frac{mV_L + V_G}{V_L V_G} K_L A t. \quad (7)$$

The slope of a plot of this logarithm vs time yields the overall liquid-phase mass transfer coefficient,  $K_L$ .

The second series of experiments was performed in a similar set-up, in which the absorption rate of pure H<sub>2</sub>S was measured with a soap film meter while an aqueous alkanolamine (methyl-diethanolamine, MDEA) was flowing through the reactor. The influence of the reaction



on the mass transport can be taken into account with an approach similar to the relations presented by Olander (1960) (see Appendix). This so-called two-film concept yields the (physical) mass transfer parameters for the membrane.

Contrary to non-wetted membranes, wetted membranes do not prevent the liquid from passing through the membrane when an overpressure in the liquid is applied. However, in the present system a small overpressure is necessary to wet the membrane completely. Complete wetting can be observed visually by the distinct colour change of the membrane. After the wetting, a liquid layer may be formed on top of the membrane. In order to avoid such a layer, the liquid was led into the cell until the gas-liquid interface was above the membrane. Next, a communicating vessel,

which was connected to the cell, was lowered with its gas-liquid interface just below the gas-membrane interface in the cell. Consequently, the liquid level in the cell lowers again but it is kept in the pores by the capillary forces. After this procedure, the gas phase was filled with pure gas.

## 4. RESULTS AND DISCUSSION

### 4.1. Non-wetted membranes

To study whether the mass transfer resistance in the liquid phase was influencing the absorption process, the mass transfer coefficient in the liquid phase was measured with the absorption of CO<sub>2</sub> in the 2 M solution of sulphuric acid. This experiment was carried out in the same way as the experiments with the wetted membranes (Section 3). The results are presented in Fig. 2 together with liquid-phase mass transfer coefficients measured without a membrane at the interface.

From Fig. 2 it can be concluded that the presence of a membrane does not influence the absolute values of the mass transfer coefficients although the situation of the interface is essentially different, a fixed vs a moving interface.

In the experiments without the membrane, the liquid stirrer speed could not be chosen above 2 rps because the flat interface was disturbed by the stirrer movement. A flat interface is essential in determining the mass transfer coefficient as the exchanging area must be known for the interpretation of the absorption data. The membrane offers the possibility to increase the stirrer speed without disturbing the mass transferring interface by which larger  $k_L$  values can be obtained. This can be useful if higher mass transfer coefficients are required, e.g. in the determination of kinetic data.

If the liquid-phase mass transfer coefficients are compared with  $K_G$  values obtained with the absorption of ammonia from nitrogen, it can be concluded that the mass transfer resistance in the liquid is not influencing the measured  $K_G$  values. This was confirmed by carrying out ammonia absorption experiments from N<sub>2</sub>, in which the liquid stirrer speed was

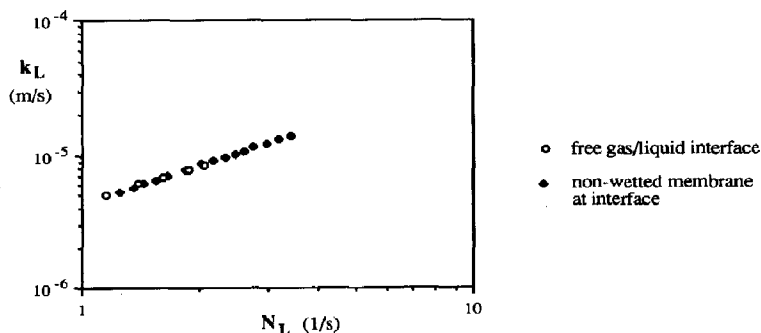


Fig. 2. Mass transfer in the liquid with and without a non-wetted membrane at the gas-liquid interface. Absorption of CO<sub>2</sub> in aqueous sulphuric acid, 2 M.

varied between 2 and 5 rps and the acid concentration from 2 to 4 M. Neither of these variations was found to influence  $K_G$ .

**4.1.1. Experiments with a batchwise-operated gas phase.** The  $K_G$  values from the absorption of diluted ammonia from nitrogen, calculated from batchwise experiments, are given in Fig. 3. As it can be seen, the mass transfer coefficient does not reach a constant value at higher stirrer speeds in the gas phase. Therefore, it must be concluded that the mass transfer resistance in the gas phase is not completely negligible. The results of layers with a different number of membranes can be used to calculate the mass transfer coefficient of the membrane. Assuming that the mass transfer coefficients of the gas phase is not influenced by the number of membranes, the mass transfer coefficient of the membrane can be derived from eq. (8):

$$\frac{1}{K_{G,A}} - \frac{1}{K_{G,B}} = \frac{1}{k_{G,A}} + \frac{n_A}{k_M} - \frac{1}{k_{G,B}} - \frac{n_B}{k_M} = \frac{n_A - n_B}{k_M} \quad (8)$$

with  $K_{G,A}$  and  $K_{G,B}$  as the overall mass transfer coefficients for systems with  $n_A$  and  $n_B$  membranes placed at the gas-liquid interface, respectively.

From the experiments with layers consisting of one, two and three membranes,  $k_M$  was calculated according to this equation. The results for all the stirrer speeds are presented in Fig. 4. At lower stirrer speeds, the contribution of the mass transfer resistance in the gas phase is too large to estimate the membrane transfer coefficient properly. However, at relatively high stirrer speeds, the calculations converge to a constant value of the membrane mass transfer coefficient when the influence of the mass transfer resistance in the gas phase becomes negligible.

**4.1.2. Experiments with a continuous gas flow.** As pointed out in Section 3.2.2, the mass transfer coefficient was calculated from the conversion of an acidic solution in a gas bubbler. To study the slip of amines

with the inert gases through the bubbler, two bubblers were used. In the second bubbler no conversion was detected. Therefore, it was concluded that under these experimental conditions the absorption of the amines was measured correctly with one gas bubbler. The influence of the gas flow through the cell was varied between  $10 \times 10^{-6}$  and  $15 \times 10^{-6}$  m<sup>3</sup>/s but no influence on the  $K_G$  value was observed.

The measured mass transfer coefficients for the absorption of MEA from He, N<sub>2</sub> and SF<sub>6</sub> at atmospheric pressures in the aqueous solution of sulphuric acid are plotted in Fig. 5(a), (b) and (c), respectively, with the number of membranes in the layer as a parameter. Although the influence of the mass transfer resistance in the gas is less pronounced as in the results discussed in the previous section, the  $k_M$  values were all calculated according to eq. (9). The results of the experiments with NH<sub>3</sub> and the different carrier gases were interpreted in the same way. The calculated membrane mass transfer coefficients are given in Table 1.

The  $k_M$  value obtained from the absorption of NH<sub>3</sub> from a mixture with N<sub>2</sub> is similar to the  $k_M$  value found with the batchwise-operated gas phase.

If the pores are so large that the Knudsen diffusion can be neglected, the membrane mass transfer coefficient should be proportional to the continuum diffusion coefficient. The porosity/tortuosity factor calculated from eq. (2) should be identical within the experimental accuracy for the six  $k_M$  values in Table 1 because for all experiments the same membrane material was used. Unfortunately, from the fourth column it can be concluded that these  $\varepsilon/\tau$  values deviate by about a factor of 2.

If the Knudsen diffusion coefficient is taken into account, the value of the constant  $Q$  [eq. (4)] is needed. In a trial-and-error procedure,  $Q$  was optimised to obtain the smallest deviation from the mean value for  $\varepsilon/\tau$ . The Knudsen and effective diffusion coefficients [eq. (3)] calculated with this value of  $Q$  are presented in the fourth and fifth column of Table 2, respectively. The optimum  $Q$  value was found to be

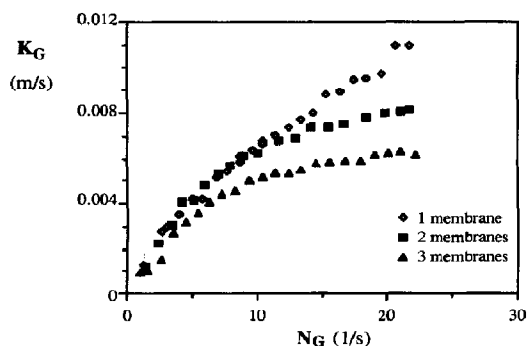


Fig. 3. Overall mass transfer coefficient in the batch experiments with different layers of non-wetted membranes at the gas-liquid interface. Absorption of NH<sub>3</sub> from a mixture with N<sub>2</sub> in aqueous sulphuric acid.

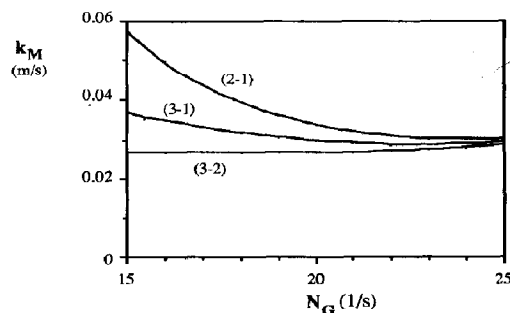


Fig. 4. Membrane mass transfer coefficient from the absorption of NH<sub>3</sub> from a mixture with N<sub>2</sub> in aqueous sulphuric acid in the batch experiments, calculated with eq. (8). With (2-1):  $n_a = 2$  and  $n_b = 1$ , (3-1):  $n_a = 3$  and  $n_b = 1$  and (3-2):  $n_a = 3$  and  $n_b = 2$ .

$1.0 \times 10^{-7}$  m, which is equal to the mean pore diameter as specified by the manufacturer of these membranes. For straight circular pores with diffuse scattering,  $Q$  is calculated to be  $\delta/3$  (Mason and

Malinauskas, 1983). Considering the sponge-like structure of this membrane (Franken, 1988) and the lack of knowledge about the scattering of the molecules on the porous structure, the estimated value

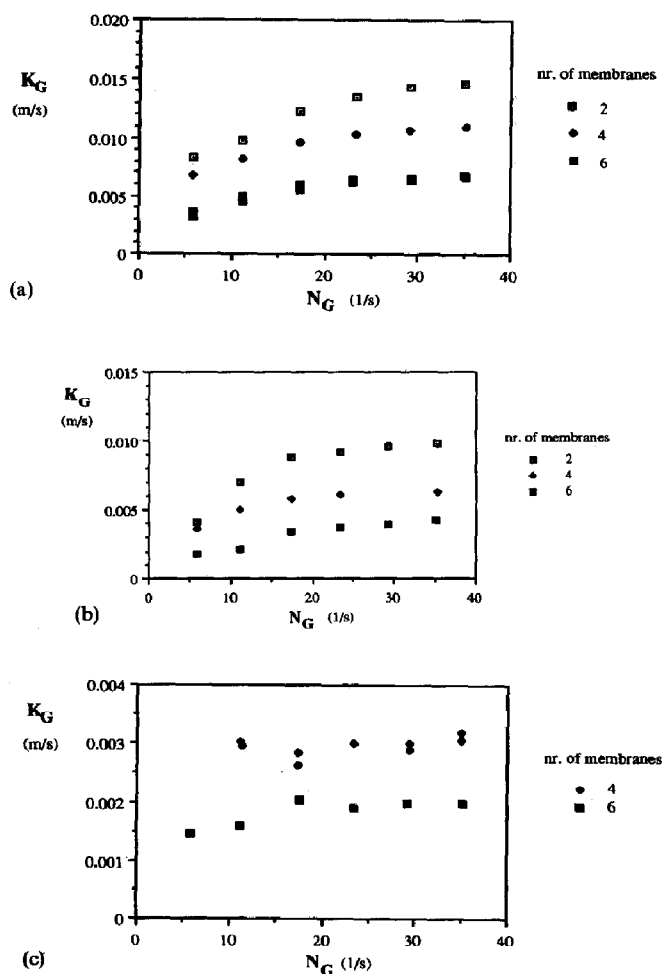


Fig. 5. Overall mass transfer coefficient in the continuous experiments with MEA absorption from: (a) He in aqueous sulphuric acid through different layers of non-wetted membranes; (b)  $N_2$  in aqueous sulphuric acid through different layers of non-wetted membranes; (c)  $SF_6$  in aqueous sulphuric acid through different layers of non-wetted membranes.

Table 1. Membrane mass transfer coefficients obtained for different gas mixtures and membrane packages relation of  $k_M$  and continuum diffusion coefficients with porosity/tortuosity factor ( $\epsilon/\tau$ )

| Gas mixture | $k_M$<br>( $10^{-2}$ m/s) | $D_{i,j}$<br>( $10^{-5}$ m <sup>2</sup> /s) | $\epsilon/\tau$ | Experimental method |
|-------------|---------------------------|---------------------------------------------|-----------------|---------------------|
| $NH_3/He$   | 7.7                       | 7.58                                        | 0.102           | Continuous gas flow |
| $NH_3/N_2$  | 3.0                       | 2.30                                        | 0.13            | Continuous gas flow |
| $NH_3/SF_6$ | 3.0                       | 2.30                                        | 0.13            | Batch gas phase     |
| $MEA/He$    | 2.2                       | 1.12                                        | 0.196           | Continuous gas flow |
| $MEA/N_2$   | 5.3                       | 4.59                                        | 0.115           | Continuous gas flow |
| $MEA/SF_6$  | 1.8                       | 1.24                                        | 0.145           | Continuous gas flow |
|             | 1.2                       | 0.54                                        | 0.222           | Continuous gas flow |

Table 2. Membrane mass transfer coefficients obtained for different gas mixtures and membrane packages: relation of  $k_M$  and effective diffusion coefficients with porosity/tortuosity factor ( $\epsilon/\tau$ )

| Gas mixture                      | $k_M$<br>( $10^{-2}$ m/s) | $D_{i,j}$<br>( $10^{-5}$ m <sup>2</sup> /s) | $D_e$<br>( $10^{-5}$ m <sup>2</sup> /s) | $D_e^\dagger$<br>( $10^{-5}$ m <sup>2</sup> /s) | $\epsilon/\tau$ | Experimental method |
|----------------------------------|---------------------------|---------------------------------------------|-----------------------------------------|-------------------------------------------------|-----------------|---------------------|
| NH <sub>3</sub> /He              | 7.7                       | 7.58                                        | 8.12                                    | 3.92                                            | 0.196           | Continuous gas flow |
| NH <sub>3</sub> /N <sub>2</sub>  | 3.0                       | 2.30                                        | 8.12                                    | 1.79                                            | 0.167           | Continuous gas flow |
| NH <sub>3</sub> /N <sub>2</sub>  | 3.0                       | 2.30                                        | 8.12                                    | 1.79                                            | 0.167           | Batch gas phase     |
| NH <sub>3</sub> /SF <sub>6</sub> | 2.2                       | 1.12                                        | 8.12                                    | 0.98                                            | 0.224           | Continuous gas flow |
| MEA/He                           | 5.3                       | 4.59                                        | 4.99                                    | 2.39                                            | 0.222           | Continuous gas flow |
| MEA/N <sub>2</sub>               | 1.8                       | 1.24                                        | 4.99                                    | 0.99                                            | 0.181           | Continuous gas flow |
| MEA/SF <sub>6</sub>              | 1.2                       | 0.54                                        | 4.99                                    | 0.49                                            | 0.246           | Continuous gas flow |

<sup>†</sup>Effective diffusion coefficient,  $D_e$ , from eq. (3).

seems realistic. The resulting tortuosity factor with this optimum  $Q$  value is equal to 3.5. This seems a normal value for porous structures with these pore diameters [see e.g. Prasad and Sirkar (1988)].

In order to investigate the applicability of a non-wetted membrane, the absorption rates in a HFMM must be compared with those that can be realised in conventional absorbers. Usually, physical absorption processes used in industry are limited by the mass transfer rates in the liquid phase. The overall mass transfer coefficient in these cases are between  $5 \times 10^{-5}$  and  $5 \times 10^{-4}$  m/s [see e.g. Westerterp *et al.* (1984)]. Adding the mass transfer resistance of the non-wetted membrane will not influence the overall mass transfer resistance significantly. Therefore, a HFMM can be very interesting for these processes because of its large specific interfacial area unless  $k_L$  values in these modules are reduced substantially.

When processes are considered in which the mass transfer is limited by the transport in the gas phase, the membrane does reduce the overall mass transfer coefficient.  $K_G$  values in conventional absorbers are in the range of 0.01–0.1 m/s [see e.g. Westerterp *et al.* (1984)], which is about the same range as determined for the membranes in the present study.

As the geometry of a HFMM usually cannot be operated at turbulent conditions, the mass transfer in the gas phase will be reduced substantially. Therefore, the overall mass transfer rate in the membrane system will be reduced also. However, as the mass transfer capacity of the absorber is very important, the high interfacial area created by the hollow-fibre membranes must compensate for the reduced overall mass transfer coefficients in order to result in an absorber with a higher capacity.

#### 4.2. Wetted membranes

The results derived from the absorption of CO<sub>2</sub> in water are presented in Fig. 6. Already at relatively low stirrer speeds the mass transfer is completely determined by the diffusion in the membrane and this membrane transfer coefficient can be derived directly from Fig. 6,  $k_M = 3.0 \times 10^{-6}$  m/s. Calculation of the tortuosity factor of the membrane from eq. (2) gives  $\tau = 4.3$ .

For the experiments with pure H<sub>2</sub>S the absorption fluxes are presented in Fig. 7. The liquid flow through

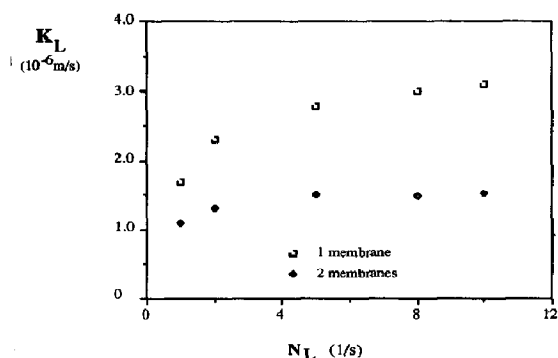


Fig. 6. Mass transfer coefficient for the absorption of CO<sub>2</sub> through a layer of water-wetted membranes as a function of stirrer speed in the liquid phase.

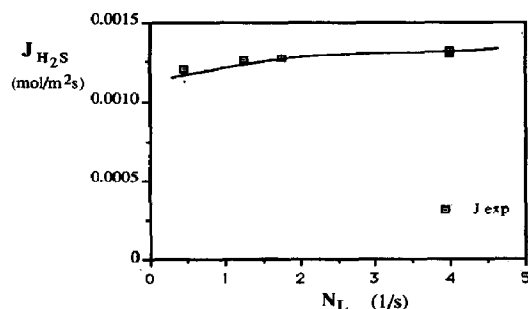


Fig. 7. Mass transfer rate of H<sub>2</sub>S through a membrane wetted with 2 M MDEA as a function of stirrer speed in the liquid phase. Drawn line calculated according to the two-film concept (see Appendix).

the cell was chosen such that it did not influence the absorption rate. With an approach similar to Olander (1960) in which the influence of the chemical reaction in both the membrane and the mass transfer film under the membrane is taken into account, the tortuosity of the pores was deduced (see Appendix A). For the present absorption system it was found that the optimum value for  $\tau$  is 3.5 and that the fluxes calculated from the model and the fitted value  $\tau = 3.5$  (drawn line in Fig. 7) agree fairly well with the experimental results.



The  $\tau$  values determined with the CO<sub>2</sub>-water and H<sub>2</sub>S-MDEA systems differ by about 20%. However, it should be mentioned that similar differences were also observed by Prasad *et al.* (1986), who used different experimental systems for liquid-liquid extraction with microporous membranes.

It can be concluded that the application of these wetted membranes in industry is less attractive than in the case of non-wetted membranes. An additional disadvantage is the fact that the membrane does not prevent the liquid to pass to the gas side of the membrane. This problem, however, can be solved by coating these membranes with a very thin hydrophobic layer ( $< 10^{-6}$  m) which does not influence the overall mass transfer coefficient (Kreulen, 1993).

Practical absorption systems operate with the overall mass transfer coefficients between  $5 \times 10^{-5}$  and  $5 \times 10^{-4}$  m/s. Introducing a wetted membrane at the interface with  $k_M$  in the order of  $10^{-6}$  m/s will reduce the overall value substantially. However, wetted membranes in a HFMM can still be useful for other reasons, e.g. selectivity (Kreulen, 1993).

### 5. CONCLUSIONS

In the present study mass transfer parameters of flat wetted and non-wetted microporous membranes, placed horizontally between the gas and liquid phase in a stirred cell, were determined.

For the measurement of  $k_M$  for the non-wetted membranes two experimental methods were used, one with a batchwise-operated gas phase, the other with a continuously flowing gas phase. No difference in the obtained values was observed with these two methods for the absorption of NH<sub>3</sub> from a mixture with N<sub>2</sub>.

To calculate the membrane mass transfer coefficient of the non-wetted membrane, eq. (9) must be used:

$$k_M = \frac{D_e \varepsilon}{\delta \tau} \quad (9)$$

In the effective diffusion coefficient, both Knudsen and continuum diffusion must be taken into account.

The structure constant,  $Q$  [eq. (4)], for the Knudsen diffusion coefficient is about  $1.0 \times 10^{-7}$  m. This value corresponds to  $\delta$ , the mean diameter of the pores in the membrane, which is close to the theoretical value of  $Q$  for cylindrical pores,  $\delta/3$ .

No difference was observed between liquid-phase mass transfer coefficients measured with and without a membrane present at the interface. The state of the gas-liquid interface (fixed or moving) does not seem critical in the absorption process.

The determination of  $k_M$  for wetted membranes was also carried out in two different ways, batchwise physical absorption and continuous chemically enhanced absorption.

With the two-film concept (see Appendix) the influence of a chemical equilibrium reaction on the mass transfer through the wetted membrane and the liquid layer under the membrane is interpreted. The calculated  $\varepsilon/\tau$  factor is in accordance with the result of the

physical absorption experiments. Therefore,  $k_M$  for a wetted membrane can also be calculated with eq. (9).

The thickness of the wetted membranes used in the present study reduces mass transfer significantly, which implies that they should not be used in regular absorption processes. However, modules with these membranes may still be interesting for absorption processes in which e.g. selectivity is an important issue.

### NOTATION

|           |                                                             |
|-----------|-------------------------------------------------------------|
| $A$       | interfacial membrane area, m <sup>2</sup>                   |
| $C$       | concentration, kmol/m <sup>3</sup>                          |
| $D$       | diffusion coefficient, m <sup>2</sup> /s                    |
| $D_{i,j}$ | diffusion coefficient in binary mixture, m <sup>2</sup> /s  |
| $D_{i,K}$ | Knudsen diffusion coefficient, m <sup>2</sup> /s            |
| $k$       | partial mass transfer coefficient, m/s                      |
| $K$       | overall mass transfer coefficient, m/s                      |
| $m$       | distribution coefficient ( $= C_L/C_G$ ), dimensionless     |
| $n$       | number of membranes, dimensionless                          |
| $N$       | stirring speed, 1/s                                         |
| $P$       | pressure, Pa                                                |
| $t$       | time, s                                                     |
| $V$       | volume, m <sup>3</sup>                                      |
| $Q$       | constant for the Knudsen diffusion coefficient [eq. (4)], m |

### Greek letters

|               |                                    |
|---------------|------------------------------------|
| $\delta$      | pore diameter, m                   |
| $\varepsilon$ | porosity, dimensionless            |
| $\tau$        | tortuosity, dimensionless          |
| $\Phi$        | volumetric flow, m <sup>3</sup> /s |

### Subscripts

|          |                 |
|----------|-----------------|
| abs      | absorbed        |
| $b$      | bulk            |
| $e$      | effective       |
| $G$      | gas phase       |
| $i$      | interface       |
| $L$      | liquid phase    |
| $M$      | membrane        |
| nw       | non-wetted      |
| w        | wetted          |
| 0        | at $t = 0$      |
| $\infty$ | at $t = \infty$ |

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#### APPENDIX: THE TWO-FILM CONCEPT FOR MASS TRANSFER AND CHEMICAL EQUILIBRIUM REACTION FOR DETERMINING THE $\epsilon/\tau$ FACTOR OF A MICROPOROUS WETTED MEMBRANE.

In this appendix the mathematical analysis of chemically enhanced absorption experiments, carried out in a system with a wetted membrane between gas and liquid phase, is reported. The mass transfer process is studied with the absorption of pure H<sub>2</sub>S into a 2 M methyl-diethanolamine (MDEA) solution.

In the approach of Olander (1960), relations are derived which describe mass transfer in gas-liquid absorption accompanied by a chemical equilibrium reaction. Because the reaction between H<sub>2</sub>S and MDEA, giving HS<sup>-</sup> and MDEAH<sup>+</sup>, can be considered as instantaneous compared to the mass transfer process, the same mathematical technique is used in the present study.

Olander developed absorption models according to the film model and the penetration model. In the present system the mass transfer takes place in two subsequent layers; first, the transfer through the liquid-filled porous membrane and, next, through the liquid layer under the membrane. It is assumed that both processes can be described with the film model, which seems logical for the mass transfer in the membrane, but for the mass transfer in the liquid layer the boundary layer is more suitable (Den Hartog and Beek, 1968). However, the fluxes described with these models differ only slightly. Therefore, the experimental fluxes were described with two films in series (see Fig. A1).

In the Olander approach the mass transfer rate is derived for the equilibrium reaction  $A + B \rightleftharpoons E + F$  (in our case:  $H_2S + MDEA \rightleftharpoons HS^- + MDEAH^+$ ) from the following equations:

$$D_A \frac{d^2[A]}{dx^2} = D_B \frac{d^2[B]}{dx^2} = -D_E \frac{d^2[E]}{dx^2} = -D_F \frac{d^2[F]}{dx^2} = -R_A$$

$$J_A = -D_A \frac{d[A]}{dx} - D_E \frac{d[E]}{dx} \quad \text{at any place in the film.}$$

Table A1. Physico-chemical data for the interpretation of H<sub>2</sub>S absorption in an aqueous solution of MDEA at 25°C

| Variable                             | Value                                     | Reference                                                      |
|--------------------------------------|-------------------------------------------|----------------------------------------------------------------|
| [MDEA] <sub>L,tot</sub>              | 2.0 × 10 <sup>3</sup> mol/m <sup>3</sup>  | Determined by Chemical Analysis,                               |
| Bulk conversion of MDEA              | 1%                                        | Present study                                                  |
| $D_{H_2S} = D_A$                     | 9.3 × 10 <sup>-10</sup> m <sup>2</sup> /s |                                                                |
| $D_{MDEA} = D_B$                     | 4.4 × 10 <sup>-10</sup> m <sup>2</sup> /s | N <sub>2</sub> O analogy, Laddha <i>et al.</i> (1981),         |
| $D_{MDEAH^+} = D_E$                  | 4.4 × 10 <sup>-10</sup> m <sup>2</sup> /s | Versteeg and van Swaaij (1988)                                 |
| $D_{HS^-} = D_F$                     | 4.4 × 10 <sup>-10</sup> m <sup>2</sup> /s |                                                                |
| $[H_2S]_{i,L} = m[H_2S]_{i,G} = A_i$ | 100 mol/m <sup>3</sup>                    |                                                                |
| $K^{\dagger}$                        | 36.1                                      | Perrin (1965), Wright and Maass (1932), Harned and Owen (1958) |

<sup>†</sup> Composed of H<sub>2</sub>S/HS<sup>-</sup>, HS<sup>-</sup>/S<sup>2-</sup>, MDEA/MDEAH<sup>+</sup> and H<sub>2</sub>O/OH<sup>-</sup> equilibria in water.

This yields

$$J_A = -\frac{D_A}{\delta} ([A]_0 - [A]_b) - \frac{D_E}{\delta} ([E]_0 - [E]_b)$$

where  $[A]_b$ ,  $[E]_0$  and  $[E]_b$  are calculated from the equilibrium constant  $K$ ,

$$K = \frac{[E][F]}{[A][B]}$$

and the loading of the amine in the bulk of the liquid. When the thickness of the film is available, the flux can be calculated.

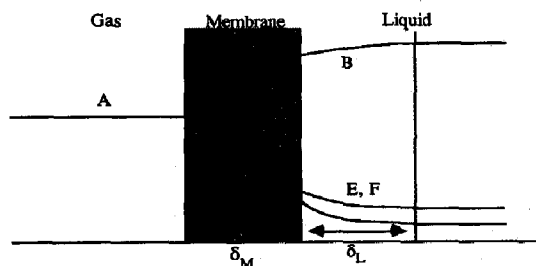


Fig. A1. Concentration profiles of mass transfer with chemical equilibrium reaction ( $A + B \rightleftharpoons E + F$ ) in a gas-membrane-liquid system.

In the two-film concept the fluxes in the two films can be solved separately with their specific boundary conditions, the concentrations at the interface of membrane and liquid. From the fact that the interface concentration is not discontinuous at the membrane-liquid interface and the fluxes in both films should be equal (steady state), the flux can be solved, provided the film thicknesses,  $K$  and  $\varepsilon/\tau$  are known. The diffusion coefficients in the membrane differ from those in the liquid phase by the factor  $\varepsilon/\tau$ , which is the membrane constant that determines the membrane mass transfer coefficient [eq. (2)]:

$$\begin{aligned} J_M &= J_L \\ \frac{\varepsilon}{\tau} \left\{ \frac{D_A}{\delta_M} ([A]_0 - [A]_1) + \frac{D_E}{\delta_M} ([E]_0 - [E]_1) \right\} \\ &= \frac{D_A}{\delta_L} ([A]_1 - [A]_2) + \frac{D_E}{\delta_L} ([E]_1 - [E]_2). \end{aligned}$$

With these relations the  $\varepsilon/\tau$  factor of the membrane is determined from the experimental mass transfer rates through the membrane (Fig. 7), physico-chemical data from Table A1 and the thickness of the liquid layer under the membrane. This last value was determined from the absorption of  $N_2O$  in the 2 M MDEA solution with a non-wetted membrane at the gas-liquid interface, see Fig. A2. The results are analogous to those of the absorption of  $CO_2$  in a sulphuric acid solution (Fig. 2). No difference could be observed between the mass transfer coefficients in the system with or without the membrane.

In a trial-and-error procedure it was found that, for  $\varepsilon/\tau = 0.7/3.5 = 0.2$ , the calculated fluxes show the smallest deviation with the experimentally determined fluxes (see Fig. 7).

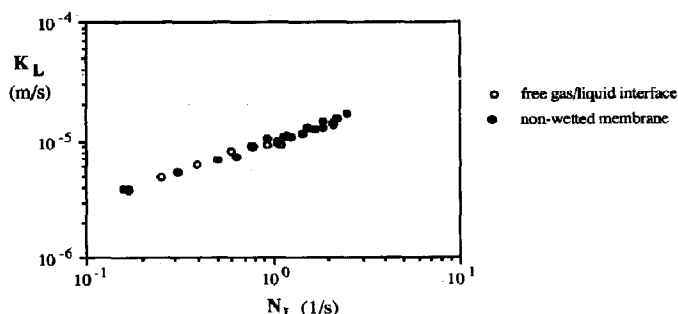


Fig. A2. Overall liquid-phase mass transfer coefficient as a function of the liquid-phase stirrer speed with and without a membrane at the gas-liquid interface. Absorption of pure  $N_2O$  in an aqueous 2.0 M MDEA solution at 25°C and atmospheric pressure.